with the metal atom. The metal complexes, by contrast, demonstrated negligible pressure effects.

Systematic pressure studies of inorganic compounds in the 1600–100-cm^{-1} region have also been started. Earlier, Lippincott *et al.* (*4, 5*) examined several inorganic molecules with pressure in the mid-infrared region, but little if any work has been done in the low-frequency region. Preliminary results (*46*) with solids in various point-group symmetries (e.g., O_h, T_d, D_{4h}, D_{3h}, C_{3v}) have indicated that external symmetry may be more important than internal (or point-group) symmetry. Certain degenerate vibrations were induced to split, while others did not. The v_4 (F-type) MnO_2 deformation vibration for $KMnO_4$ at ~ 400 cm^{-1} is seen as a doublet at ambient pressure. The doublet has been attributed to a lowered symmetry (probably C_{3v}). Differentiation between the two species is normally difficult. Figure 8 illustrates the effect of pressure on the doublet. It is observed that the low-frequency band splits into a doublet and that the high-frequency band decreases in intensity. Under pressure, the degeneracy of the F vibration (v_4) is completely removed. It is concluded that in the spectrum of $KMnO_4$ at ambient pressure, the low-frequency band is the E species and the high-frequency band is the A_1 species. The higher frequency (v_3–F type), under twice the pressure of that used for the v_4 vibration, failed to split. At ambient
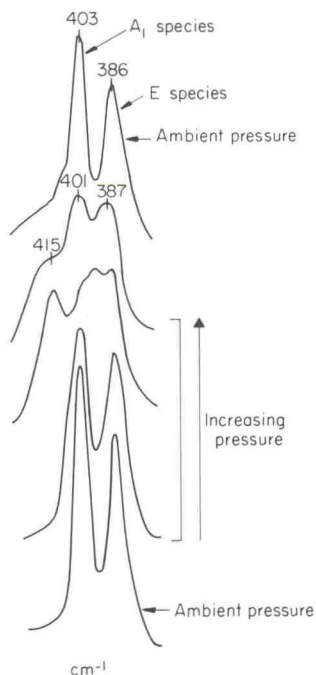

FIG. 8. The behavior of the $\delta(MnO_2)$ vibration in $KMnO_4$ with pressure (diamond cell).

pressure, 'his band is a singlet. The v_1 vibration, normally forbidden in the infrared, disappears with pressure. Thus, the results cannot be attributed to a further lowering of the symmetry of the solid under pressure. A possible explanation is offered in a later section.

In a recent study of complexes of the type L_2MX_2 (tetrahedral monomer versus octahedral polymer), where M is cobalt, X is halide, and L is pyridine or substituted pyridines, the differentiation of a bridged vibration, $v_b(CoX)$, from a terminal vibration, $v_t(CoX)$, was made on the basis of pressure measurements (47). The most pressure-sensitive bands (in terms of a blue shift) in the spectrum of the polymer were the $v_b(CoX)$ vibrations, which should have pseudolattice-like behavior.

The pressure gradient existing in the multiple-anvil diamond cell has already been discussed. In an attempt to eliminate as much of the gradient as possible, experiments with molybdenum steel gaskets were made. It has been experienced that applying pressure on a solid with a gasket does not give hydrostatic pressures. However, using a gasket with the solid HgI_2, adding a drop of Nujol, and then applying pressure gave what appeared under the microscope to be a single pressure (48). Similar results were obtained recently by Davies (24) with nickel dimethylglyoxime using other organic solvents. Under these conditions, the use of a liquid having a freezing point at a known pressure can also give a pressure calibration point as well as a hydrostatic pressure.

D. Conclusions

Four types of pressure-sensitivity for molecular vibrations have been observed thus far in the course of pressure studies on various modes of vibrations: (1) a broadening and a decrease in peak intensity of vibrations; (2) the doubling of absorption bands; (3) the splitting of degenerate vibrations; (4) frequency shifts in bands. Some of these effects have been observed for both external and internal vibrations.

1. EXTERNAL VIBRATIONS

The effects of pressure on external vibrations have been demonstrated. Both the longitudinal and transverse optical modes are seen to shift in compressible ionic solids. In all cases studied thus far, the shift is in the direction of higher frequency in agreement with low-temperature shifts. However, the pressure shifts may be considerable when compared with the temperature shifts. It is known that the temperature dependence of the peak position and half-width of lattice vibrational modes consist of two contributions: (1) the purely volume-dependent contribution; and (2) the contribution from the various anharmonic (cubic and higher) terms in the potential